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Isotopic and geochemical tracers for U(VI) reduction and U mobility at an *in situ* recovery U mine

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ABSTRACT

In situ recovery (ISR) uranium (U) mining mobilizes U in its oxidized hexavalent form (U(VI)) by oxidative dissolution of U from the roll-front U deposits. Post-mining natural attenuation of residual U(VI) at ISR mines is a potential remediation strategy. Detection and monitoring of naturally occurring reducing subsurface environments are important for successful implementation of this remediation scheme. We used the isotopic tracers $^{238}\text{U}/^{235}\text{U}$ ($\delta^{238}\text{U}$), $^{234}\text{U}/^{238}\text{U}$ activity ratio, and $^{34}\text{S}/^{32}\text{S}$ ($\delta^{34}\text{S}$), and geochemical measurements of U ore and groundwater collected from 32 wells located within, upgradient and downgradient of a roll-front U deposit to detect U(VI) reduction and U mobility at an ISR mining site at Rosita, TX, USA. The $\delta^{238}\text{U}$ in Rosita groundwater varies from 0.61‰ to -2.49‰, with a trend toward lower $\delta^{238}\text{U}$ in downgradient wells. The concurrent decrease in U(VI) concentration and $\delta^{238}\text{U}$ with an ϵ of $0.48\text{‰} \pm 0.08\text{‰}$ is indicative of naturally occurring reducing environments conducive to U(VI) reduction. Additionally, characteristic $^{234}\text{U}/^{238}\text{U}$ activity ratio and $\delta^{34}\text{S}$ values may also be used to trace the mobility of the ore zone groundwater after mining has ended. These results support the use of U isotope-based detection of natural attenuation of U(VI) at Rosita and other similar ISR mining sites.

Introduction

In situ recovery (ISR) of uranium (U) is a widely used subsurface mining technique by which U is extracted via oxidative dissolution of sandstone-hosted U ore deposits^{1,2}. The ISR mining approach is becoming increasingly common³ as it enables economic recovery of low-grade ores, does not generate tailings, and has a relatively low carbon footprint³⁻⁵. In 2012, ISR mining accounted for ~45% of global U production³. In low temperature sandstone-hosted ore deposits, U primarily occurs in the tetravalent oxidation state (i.e., U(IV)) in minerals such as uraninite or coffinite^{6,7}. The mining process capitalizes on the high permeability of the ore bearing sandstone aquifer and involves injection of a lixiviant containing oxidants (e.g., dissolved oxygen, hydrogen peroxide, sulfuric acid) and complexing agents (e.g., HCO_3^-) that oxidize U(IV) to highly soluble U(VI), which forms stable uranyl carbonate complexes in the mining solution. However, ISR activity mobilizes U as chemically toxic and bioavailable U(VI), which may potentially contaminate water resources downgradient of ISR mines when advected by groundwater after mining ceases.

Redox dependent solubility of U controls the mobility of U in the subsurface and influences a major part of low-temperature U cycling, including the formation economic U deposits. For instance, sandstone-hosted U ore deposits, comprising almost 90% of all known U resources in the United States⁸ and ~25% worldwide⁹, originate from the reduction of dissolved U(VI) to insoluble U(IV) when U-bearing groundwaters encounter reducing conditions. A sub-type of sandstone-hosted U ores, crescent-shaped roll-front deposits, are formed perpendicular to the groundwater flow direction at the interface between the reduced and oxidized portions of the aquifers⁹⁻¹². The redox gradient from oxidizing to progressively reducing conditions is a result of abiotic reductants (e.g., Fe(II)-bearing minerals, organic matter, aqueous Fe(II) and H_2S , CH_4) and/or microbial activity⁸. The ISR mining perturbs the prevailing redox conditions within these

deposits and creates artificially oxidizing conditions. However, naturally occurring reducing environments within and downgradient of the ore deposits may induce reductive immobilization of the U(VI) generated by ISR activity during mining fluid excursions and once the natural hydrology is restored. If effective, this post-mining natural attenuation of U(VI) in groundwater would provide an inexpensive remediation strategy at ISR sites.

Naturally occurring U isotopes (e.g., ^{238}U , ^{235}U) may serve as indicators of environments conducive to U(VI) reduction and U mobilization. Reduction of U(VI) to U(IV) induces a mass independent isotopic fractionation due to a mechanism known as the nuclear volume effect leading to the preferential enrichment of ^{238}U in the U(IV) products¹³⁻¹⁵. Thus, U(VI) reduction results in progressively decreasing $^{238}\text{U}/^{235}\text{U}$ in the remaining aqueous U(VI). This isotopic fractionation effect was first suggested from theoretical calculations^{14,16}, and later confirmed by observations of ^{238}U enrichment in geological samples (e.g., black shales, and roll-front deposits)¹⁷⁻²¹ and field scale and laboratory batch incubation experiments on U(VI) bioreduction^{22,23}. The magnitude of the isotopic fractionation is often expressed by an isotopic enrichment factor, ϵ ($\epsilon=1000*(\alpha-1)$; $\alpha = (^{238}\text{U}/^{235}\text{U})_{\text{Product}}/(^{238}\text{U}/^{235}\text{U})_{\text{Reactant}}$). Non-reductive processes (e.g., adsorption, dilution) leading to U(VI) concentration decrease do not significantly affect the U isotope ratios in aqueous systems²⁴. Therefore, $^{238}\text{U}/^{235}\text{U}$ in groundwater is an effective indicator of U(VI) reduction.

Co-existing sulfur isotopes ($\delta^{34}\text{S}$) may also be used to assess the post-mining redox state of the ISR sites. The “nose” of the roll-front deposits at many sites contains abundant sulfide minerals (i.e., Mo- and Fe-sulfides)²⁵⁻³¹. Oxidative dissolution of the sulfide minerals during ISR mining generates SO_4^{2-} and hence the S isotopic composition of SO_4^{2-} can be particularly useful to detect both mineral dissolution and post-mining sulfate reduction in groundwater. Sulfate reduction

leads to preferential accumulation of lighter S isotopes (^{32}S) in sulfide (i.e., reaction product) rendering the residual sulfate in groundwater enriched in heavier ^{34}S . Both abiotic and microbial sulfate reduction to sulfide induce large fractionations; the ϵ_{S} values (defined similarly as in the above equation used for U) for abiotic and microbial sulfate reduction are 22‰ and 6-46‰, respectively^{32,33}. In contrast, oxidation of sulfide minerals to sulfate induces a smaller fractionation (<5‰) where the aqueous sulfate progressively acquires the isotopic signature of the source sulfide³². Thus, S isotope ratios in post-mining groundwater can serve as a tracer for mining fluid resulting from mineral dissolution, as well as an indicator of aqueous sulfate reduction, if any.

The $^{234}\text{U}/^{238}\text{U}$ activity ratios, expressed as ($^{234}\text{U}/^{238}\text{U}$), in groundwater may also be used as a tracer for U mobility in the subsurface³⁴. The ^{234}U is the daughter of the short-lived decay product ^{234}Th ($t_{1/2} = 24.1\text{d}$) produced by α decay of ^{238}U . In undisturbed U deposits older than ~ 1 million years, ($^{234}\text{U}/^{238}\text{U}$) should approach secular equilibrium (i.e., ($^{234}\text{U}/^{238}\text{U}$) = 1). ($^{234}\text{U}/^{238}\text{U}$) in sediments and groundwater often deviates from secular equilibrium due to the complex interplay between α -recoil and dissolution of U minerals³⁵. The emission of an α -particle causes the daughter product ^{234}Th to recoil a distance of ~ 30 nm in the lattice of silicate minerals^{36,37}. When the grain size is sufficiently small, this recoil may cause the ejection of ^{234}Th and the daughter product ^{234}U into the surrounding medium. In larger particles, the α -recoil tends to concentrate ^{234}U at sites damaged by the decay process causing ^{234}U to be preferentially leached during oxidative dissolution. Thus, the U mineral undergoing α -decay acquires a ($^{234}\text{U}/^{238}\text{U}$) less than unity, whereas the ($^{234}\text{U}/^{238}\text{U}$) of the surrounding groundwater is typically greater than 1^{37,38}. However, in open systems where the dissolved U is continuously removed, ($^{234}\text{U}/^{238}\text{U}$) in the groundwater may evolve to be lower than the secular equilibrium value³⁹. A characterization

of the ($^{234}\text{U}/^{238}\text{U}$) signature of the ore and the post-mining groundwater is required for successful use of ($^{234}\text{U}/^{238}\text{U}$) activity ratios as tracer for U mobility at ISR sites.

Here, we report high precision measurements of $\delta^{238}\text{U}$, ($^{234}\text{U}/^{238}\text{U}$) and $\delta^{34}\text{S}$ and the elemental composition groundwater samples collected at an alkaline ISR mine (see Supporting Information) from upgradient, within and downgradient of a roll-front type U deposit at Rosita, Texas, U.S.A. We also report U and S isotope measurements of U ore collected from an adjacent un-mined part of the roll-front. Our objectives are to i) detect naturally occurring reducing environments conducive to U(VI) reduction through isotopic and geochemical measurements and, ii) characterize the ($^{234}\text{U}/^{238}\text{U}$) of the U ore and the groundwater in order to use U activity ratios as a tracer for the migration of post-mining groundwater from the ore zone.

Materials and Methods

The study site is located at Rosita (Duval County), TX, USA, in the Texas coastal plain region. The ore deposit at the study site is divided into four mining units or production area authorizations (PAAs) - PAA1, PAA2, PAA3 and yet to be mined PAA4 (Figure 1). The mining was carried out using the site groundwater fortified with NaHCO_3 and/or CO_2 (g) and oxidants (O_2 , H_2O_2). We collected groundwater samples from 32 wells located upgradient, within, and downgradient of the roll-front ore in May 2013 (Figure 1). We obtained a sediment core from the ore zone (borehole OZCH3, adjacent to BL 39) within the un-mined PAA4 area (Figure 1). Details of the site background, lithology (Figure S1), mining history, methods for sample collection and, major ion and trace element analysis are provided in the Supporting Information.

Isotopic Analyses. The $^{238}\text{U}/^{235}\text{U}$ measurements in groundwater and digested ore samples were performed at the Stanford ICP-MS/TIMS Facility, Stanford University, using a Nu Plasma multi-collector - inductively coupled plasma mass spectrometer (MC-ICPMS) following the

132 methods described in references^{17,22-24}. All samples were purified using the ion exchange resin
 133 UTEVA (Eichrom Technologies, LLC) prior to isotopic measurements. The measured $^{238}\text{U}/^{235}\text{U}$
 134 ratios are expressed as $\delta^{238}\text{U}$ relative to the U isotope standard CRM 145, defined by

$$135 \quad \delta^{238}\text{U} = \left[\frac{(^{238}\text{U}/^{235}\text{U})_{\text{sample}}}{(^{238}\text{U}/^{235}\text{U})_{\text{CRM145-A}}} - 1 \right] \times 1000\text{‰} \quad (1)$$

136 Analytical uncertainty of the isotope measurements was $\pm 0.09\text{‰}$ determined as twice the root
 137 mean square difference for 10 pairs of duplicate sample preparations.

138 The ($^{234}\text{U}/^{238}\text{U}$) values were measured at the Center for Isotope Geochemistry, Lawrence
 139 Berkeley National Laboratory using an IsoProbe MC-ICPMS (GV Instruments) following the
 140 method described in ref⁴⁰. Prior to isotopic analyses, the samples were purified via ion-exchange
 141 chromatography. The analytical precision (2σ) of the ($^{234}\text{U}/^{238}\text{U}$) was $<0.2\text{‰}$.

142 Sulfur isotope ratios in groundwater and ore samples were measured at the Laboratory for
 143 Environmental and Sedimentary Isotope Geochemistry, University of California, Berkeley on a
 144 Eurovector model 3028 elemental analyzer interfaced with a GV Isoprime isotope ratio mass
 145 spectrometer. Details on the sample preparation and measurement technique can be found in
 146 ref⁴¹. The analytical uncertainty (2σ) for the isotope measurements was 0.15‰ determined from
 147 the long-term measurements of S isotope standard NBS 127 and in house standards. We report
 148 the measured $^{34}\text{S}/^{32}\text{S}$ isotope ratios as $\delta^{34}\text{S}$, relative to that of the standard reference material
 149 Canyon Diablo Troilite, defined as

$$150 \quad \delta^{34}\text{S} = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{CDT}}} - 1 \right] \times 1000\text{‰} \quad (2)$$

151 We measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in groundwater samples with $>0.1 \text{ mg/L NO}_3^-$ to detect
 152 any possible microbial denitrification. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- were measured using a
 153 modified version of the microbial denitrification technique described in refs^{42,43}. Briefly, N_2O
 154 gas evolved following reduction of nitrate by *Pseudomonas aureofaciens* (ATCC 13985) was

measured in continuous flow mode using a GV Instruments Isoprime isotope ratio mass spectrometer (GV Instruments, Manchester, UK) coupled to a TraceGas peripheral instrument. Calibration was performed based on standards IAEA-NO-3, USGS32 and USGS34. Precision was typically ± 0.25 ‰ for $\delta^{15}\text{N}$ and ± 0.90 ‰ for $\delta^{18}\text{O}$.

The details of ore digestion procedure, major ion and trace element measurement methods, and Sr isotope measurements in Rosita groundwater are provided in the Supporting Information.

Results and Discussion

Geochemistry and isotope geochemistry of Rosita groundwater. The major ion and trace element chemistry of the groundwater samples are shown in Table S1. The pH of Rosita groundwater samples measured during sample collection varies from 6.56 to 7.36. The dissolved organic carbon in the groundwater ranges from 0.66 mg/L to 6.28 mg/L with a median value of 1.2 mg/L. In general, the groundwater samples are characterized by high concentrations of Na^+ (156 - 472 mg/L), Ca^{2+} (72 - 391 mg/L), Cl^- (341 - 1254 mg/L), HCO_3^- (190 - 379 mg/L), SO_4^{2-} (66 - 653 mg/L, median concentration 243 mg/L) and total dissolved solids (1045 – 3188 mg/L). U(VI) concentrations in the groundwater samples range from 0.001 mg/L to 12.9 mg/L with the highest concentrations observed in the samples collected from the previously-mined ore zone, particularly in samples BL 28, BL 29, and BL 34 from the most recently mined, and as of yet unrestored, PAA3. The redox potential (Eh) measured in groundwater samples varies from 94.2 mV to -105.5 mV. Some groundwater samples also contain a minor amount of dissolved Fe (up to 3.0 mg/L), Mn (up to 0.56 mg/L) and NO_3^- (up to 29.8 mg/L) (Table S1, Figure S2). In addition, the samples from both previously mined and un-mined ore zone BL wells contain dissolved Mo (0.003 – 3.41 mg/L; median concentration 0.39 mg/L).

177 The isotopic compositions of the groundwater samples are shown in Table S2. A wide range of
178 $\delta^{238}\text{U}$ values from 0.61‰ to -2.49‰ is observed in Rosita groundwater (Figure 2). Most of the
179 ore zone groundwater samples are characterized by high $\delta^{238}\text{U}$ values ($\sim 0.0\text{‰} < \delta^{238}\text{U} < 0.61\text{‰}$),
180 whereas the $\delta^{238}\text{U}$ of the groundwater from recently mined PAA3 and most of the upgradient
181 wells are close to 0.0‰. In contrast, most of the downgradient water samples are highly depleted
182 in ^{238}U , exhibiting negative $\delta^{238}\text{U}$ values in the range -0.15‰ to -2.49‰. In a subset of samples,
183 a systematic decrease in $\delta^{238}\text{U}$ values is observed with decreasing U(VI) concentration that
184 conforms to a Rayleigh distillation model with an ϵ of $0.48\text{‰} \pm 0.08\text{‰}$ (Figure S3).

185 The ($^{234}\text{U}/^{238}\text{U}$) in the groundwater samples from previously mined and un-mined PAAs varies
186 from 0.72 to 2.23 (Table S2, Figure 3). All ore zone wells, except BL 8, in the mined part of the
187 roll-front exhibits a narrow range of ($^{234}\text{U}/^{238}\text{U}$), with an average value of ~ 0.75 . Except for five
188 samples (MW 53, MW 75, MW 102, MW 129, and MW 137), ($^{234}\text{U}/^{238}\text{U}$) in both upgradient and
189 downgradient wells are less than unity (Figure 3). In all transects (except the one containing BL
190 8) the ($^{234}\text{U}/^{238}\text{U}$) is lowest in the ore zone and higher, approaching secular equilibrium, in both
191 the upgradient and downgradient wells.

192 We observed a wide range of $\delta^{34}\text{S}$ (11.8‰ to -19.9‰) in aqueous sulfate from groundwater
193 samples (Table S2). Most of the ore zone wells from previously mined PAA1, PAA2, and PAA3,
194 except BL 8, BL 17, and BL 10, are depleted in aqueous ^{34}S (i.e. $\delta^{34}\text{S} \ll 0.0\text{‰}$). Among these,
195 the most depleted $\delta^{34}\text{S}$ values are observed in samples from the most recently mined PAA3.
196 Most upgradient and downgradient samples, in contrast, have $\delta^{34}\text{S}$ near 0.0‰ or more enriched
197 values up to $\sim 12\text{‰}$ (except in MW 25 and MW 85). In the un-mined PAA4, $\delta^{34}\text{S}$ values in all
198 samples (upgradient, ore zone, and downgradient) are enriched ($> 0.0\text{‰}$) and fall within a

narrow range (3.17‰ to 6.56‰). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in groundwater from the mined PAA1, PAA2, and PAA3, varies from 0.7076 to 0.7081 (Figure S4).

Isotope geochemistry of Rosita U ore. Isotopic analyses of Rosita U ore, collected from the borehole OZCH3, in the un-mined PAA4 area (Figure 1), are provided in Table S2. We analyzed samples from four discrete depths across the uranium rich zones as identified by prompt fission neutron measurements in the borehole. The U ore is isotopically heterogeneous with $\delta^{238}\text{U}$ values from -0.16‰ to -1.33‰ and concentrations ranging from 38 mg kg^{-1} to 250 mg kg^{-1} . Despite the variability in $\delta^{238}\text{U}$, the weighted average $\delta^{238}\text{U}$ for the U ore is -0.31‰ . The $(^{234}\text{U}/^{238}\text{U})$ values are also extremely low (0.69 to 0.82; average 0.76) in these samples, and tend to increase with depth. We observed highly depleted $\delta^{34}\text{S}$ values (-28.5‰ to -38.8‰) in the ore. There is no clear relationship between depth and $\delta^{238}\text{U}$ or $\delta^{34}\text{S}$.

Fractionation of ^{238}U and U(VI) removal in reducing zones. The systematic decrease in $\delta^{238}\text{U}$ with U(VI) concentration in Rosita groundwater suggest naturally occurring U(VI) reduction as the major U removal process, particularly in areas downgradient of the roll-front. Correlation between the $\delta^{238}\text{U}$ and concentration exclude dilution as the explanation for low U concentrations in the downgradient region (Figure 2). Dissolution of the ore could affect the $\delta^{238}\text{U}$ in Rosita groundwater but appears negligible for the following reason. The $\delta^{238}\text{U}$ values (as low as -2.49‰) in groundwater from several downgradient monitoring wells are much more depleted than those observed in the U ore (Figure 2). Therefore dissolution of U ore cannot solely account for the observed distribution of U isotopic fractionation in the downgradient water samples. Adsorption as the major non-reductive U(VI) removal process is unlikely due to the abundance of dissolved calcium ($72 - 391\text{ mg/L}$ or $1.8 - 9.8\text{ mM}$) and HCO_3^- ($190 - 379\text{ mg/L}$ or $3.1 - 6.2\text{ mM}$) in the site groundwater. Under these conditions, calcium-uranyl-carbonate

222 complexes ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0_{\text{aq}}$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) become dominant U species⁴⁴ at near-neutral
223 to slightly alkaline pH and substantially decrease the adsorption of U(VI) onto mineral grains<sup>45-
224 51</sup>. A minor amount of adsorption of U(VI) may still occur, but adsorption-desorption does not
225 cause U isotope fractionation²⁴. In addition, U(VI) reduction is uninhibited and
226 thermodynamically favorable at high HCO_3^- and Ca^{2+} .^{52,53}

227 The only mechanism known to induce large U isotope fractionation is the reduction of U(VI)
228 to U(IV). The overall variation of $\delta^{238}\text{U}$ in Rosita groundwater is 3.1‰, which is a factor of 3
229 higher than that observed during U(VI) bioremediation experiments at U.S. Department of
230 Energy's Integrated Field Research Challenge (IFRC) site at Rifle, Colorado, USA²² and similar
231 to the overall change in $\delta^{238}\text{U}$ reported for groundwater samples from the Pepegona sandstone-
232 hosted U deposit, Australia²¹, and for microbial reduction of U(VI) in batch incubation
233 experiments²³. Furthermore, for all transects, except the one containing BL8, in the previously
234 mined PAAs, the $\delta^{238}\text{U}$ and U(VI) concentrations decrease along the putative redox gradient
235 from the ore zone to downgradient monitoring wells, suggesting greater extents of U(VI)
236 reduction and concomitant isotopic fractionation in (presumably) more reducing environments
237 downgradient of the ore zone.

238 Additional geochemical data from the previously mined PAAs are consistent with the reducing
239 environments identified based on the U isotope ratios. Along a groundwater flow path, a
240 sequential zonation of terminal electron acceptors (e.g., O_2 , NO_3^- , Mn(IV)) based on energetic
241 favorability of microbially-mediated redox processes is often observed in aquifers^{54,55}. The
242 sequence of reduction depends on the prevailing redox potential (Eh) and is usually as follows:
243 $\text{O}_2 > \text{NO}_3^- > \text{Mn(IV)} > \text{Fe(III)} > \text{SO}_4^{2-} > \text{CO}_2$. Under certain conditions, the concentrations of the

soluble products of these reduction reactions (i.e., Mn^{2+} or Fe^{2+}) may be used to identify the terminal electron accepting process (i.e., Mn(IV) or Fe(III) reduction)⁵⁴.

We observe a decrease in NO_3^- concentrations along the hydraulic gradient excluding the wells located downgradient of mapped gaps in the ore deposit that suggest heterogeneities in flow and mineral distribution (MW 32, MW 102, MW 103, MW 137); (Figure 1). Despite the absence of a clear trend of decreasing NO_3^- concentrations with increasing $\delta^{15}\text{N}$ -nitrate, the $\delta^{18}\text{O}$ -nitrate vs. $\delta^{15}\text{N}$ -nitrate plot shows a linear relation ($r^2 = 0.77$, $n = 11$) with a slope ($\Delta\delta^{18}\text{O}/\Delta\delta^{15}\text{N}$) of 0.73 ± 0.13 similar to that characteristic of microbial denitrification⁵⁶⁻⁶¹, particularly in the upgradient wells in the previously mined parts of the site (Figure S5). The abovementioned gaps in the ore deposit at the southernmost part of PAA2 and in PAA3 (Figure 1) enables the nitrate-rich groundwater to arrive at the downgradient wells MW 32, MW 102, MW 103, and MW 137. In this process, the upgradient water also dilutes the U(VI) concentrations in the downgradient wells on its flow path. Dissolved Mn (>0.05 mg/L) and Fe (>0.1 mg/L) concentrations in Rosita groundwater additionally suggest localized zones of Mn(IV) and Fe(III) reduction in PAA1, PAA2, and PAA3 (Figure S2).

The general trend in Eh coincides with the distribution of NO_3^- , Fe and Mn concentrations in Rosita groundwater. The Eh values (94.2 mV to -105.5 mV) in Rosita groundwater suggest a wide range of likely redox reactions such as denitrification, Mn(IV), Fe(III), and U(VI) reduction (occurring below 0.0 mV at pH 7)⁴⁴, but are higher than that required for sulfate reduction (≤ -200 mV)^{44,54,62,63}. We observe an apparent trend of decreasing Eh values downgradient of the ore zone in the previously mined PAAs; high Eh (-30 mV to + 90 mV) are mostly associated with the upgradient and ore zone wells where various degrees of oxidation is expected (Figure S2). Most of the downgradient wells (except MW 32, MW 102, MW 103, MW 137) in all

previously mined PAAs show low to very low Eh values suggesting reducing environments. At near-neutral pH, the zones of Fe(III) reduction along with very low Eh values (~ -100 mV) suggest the presence of reducing environments favorable for U(VI) reduction^{44,63}.

The concurrent decrease of $\delta^{238}\text{U}$ and U(VI) in groundwater along the hydraulic gradient can be modeled using a Rayleigh distillation relationship. In our calculation of ϵ , we excluded the wells affected by dilution, either by the upgradient water as evident from the nitrate plume (e.g., at the boundary of PAA1 and PAA2) or by the most recent mining activity in PAA3. We also excluded MW 149 (PAA4), in which ^{238}U enrichment ($\delta^{238}\text{U} = 0.48\text{‰}$) similar to the corresponding ore zone well BL 39 suggests a lack of U(VI) reduction. The U(VI) data from the wells affected by non-reductive U removal, dilution or dissolution would lead to an error in estimating the relationship between the remaining unreduced U(VI) and the accompanying $\delta^{238}\text{U}$ and thus in the estimation of the ϵ in the Rayleigh distillation model. The fit of the data from the 14 remaining wells, including the PAA4 wells, yields an ϵ value of 0.48‰ (Figure S3). The magnitude of U isotope fractionation (ϵ) in Rosita groundwater is very similar to that determined for microbial U(VI) at the Rifle biostimulation site ($\epsilon \approx 0.46\text{‰}$)²², and about a factor of two less than that observed during microbial U(VI) reduction in batch incubation experiments ($\epsilon \approx 1.0\text{‰}$)²³. Because Rayleigh distillation models presuppose a closed system with no back reaction, applicability of these models to determine the magnitude of U isotope fractionation during U(VI) reduction in aquifers is somewhat uncertain and hydrodynamic dispersion and diffusion can lead to underestimation of the fractionation factors⁶⁴. In addition, field scale chemical heterogeneity at the Rifle biostimulation site and at Rosita might have resulted in a diffusive limitation between the isolated zones of U(VI) reduction leading to less apparent fractionation compared to that observed during U(VI) reduction in well-mixed batch incubation

experiments^{65,66}. Alternatively, different U(VI) reduction mechanism(s) at Rosita might have generated the difference in ϵ with previously published studies.

Several groundwater samples from the ore zone and upgradient wells, both from the previously mined and un-mined parts of the site, show ^{238}U enrichment ($0.0\text{‰} < \delta^{238}\text{U} < 0.61\text{‰}$) relative to the U ore collected from OZCH-3 in PAA4. For example, $\delta^{238}\text{U}$ in groundwater from BL 39 from un-mined PAA4 is much higher than that of the U ore ($\delta^{238}\text{U}$ at highest U concentration = -0.22‰) obtained from the adjacent borehole OZCH-3. The U isotope fractionation in this case is opposite to that observed during U(VI) reduction or equilibrium isotopic fractionation between U(IV) and U(VI) (i.e., ^{235}U enrichment in the dissolved U(VI)).

The mechanism(s) responsible for enrichment of ^{238}U in the groundwater is unclear. It is unlikely that U mineral dissolution gives rise to these anomalous $\delta^{238}\text{U}$ in the groundwater as several recent studies demonstrated lack of isotope fractionation during progressive leaching of U minerals¹⁸⁻²⁰. However, it is not known whether oxidation of U(IV) to U(VI) during incongruent dissolution of U minerals induces any isotopic fractionation. Brennecka et al. (2011) reported a small isotopic fractionation ($\sim 0.2\text{‰}$) during adsorption of U(VI) on Mn-oxyhydroxides in experiments at pH ~ 5 using a diluted U solution equilibrated with atmospheric CO_2 , where preferential adsorption of ^{235}U led to an enrichment of ^{238}U in the remaining dissolved U(VI)⁶⁷. These experimental conditions greatly differ from the near neutral to slightly alkaline Rosita groundwater with abundant dissolved Ca ($> 72 \text{ mg/L}$ or 1.8 mM) and bicarbonate ($> 190 \text{ mg/L}$ or 3.1 mM), which should render the adsorption of U(VI) less effective and minor. Because U(VI) reduction produces ^{238}U enriched U(IV) minerals, remobilization of isotopically heavy U ore ($\delta^{238}\text{U} > 0.0\text{‰}$) resulting from prior U redox cycling may produce ^{238}U enriched groundwater. The $\delta^{238}\text{U}$ of the U ore from a single core (OZCH-3 in PAA4) does not show the

enriched values expected for U that has been enriched by prior redox cycling; however, we cannot assess the spatial variability in the extent of ^{238}U enrichment based on the limited measurements. Therefore, further investigation is required to determine ^{238}U enrichment mechanisms.

U attenuation and reducing environments in un-mined PAA4. The geochemical and isotope data from groundwater and sediment samples from the un-mined PAA4 area provide some key insights into the naturally occurring processes that can be used as a proxy for the pre-mining U cycling at the study site. In the un-mined area, dissolved oxidants (e.g., oxygen, nitrate) in recharge groundwater interact with the reducing environments in and downgradient of the ore deposit. This process should lead to consumption of the oxidants as the packet of water moves through progressively more reduced zones. Our results showed this general trend despite spatial heterogeneity at the study site. For example, NO_3^- concentrations decreased from 12-15 mg/L in the upgradient water (MW 158, MW 154) to below detection (< 0.1 mg/L) in the ore zone or in the downgradient samples in PAA4 (Figure 1, Table S1). In addition, elevated concentrations of dissolved Fe and Mn (Table S1) in the ore zone and downgradient wells compared to those in the upgradient wells suggest subsurface environments conducive to Fe(III) and Mn(IV) reduction. The distribution of U(VI) in groundwater samples is heterogeneous; U dissolution is suggested by elevated U(VI) in the upgradient wells in both transects and in BL 39 (U(VI) = 1.47 mg/L) whereas the groundwater samples from the downgradient wells are characterized by very low U(VI) (< 0.008 mg/L). This decrease in U(VI) in the downgradient water presumably results from U(VI) reduction somewhere between the ore deposit and the downgradient location.

Although U(VI) concentration data provide no clear information on the distribution of reducing environments, U isotope ratios in groundwater may indicate U(VI) reduction in the PAA4 area. The U(VI) in samples from the eastern transect (MW 158, BL 36, MW 144) becomes increasingly enriched in ^{235}U (lowered $\delta^{238}\text{U}$ from -0.08‰ to -1.91‰). Highly depleted $\delta^{238}\text{U}$ (-1.91‰) observed in the sample from MW 144 cannot be produced by dissolution of the isotopically light fraction ($\delta^{238}\text{U} = -1.33\text{‰}$) of the ore. This suggests progressive U(VI) reduction along this transect. In contrast, $\delta^{238}\text{U}$ of all groundwater samples from the western transect (MW 154, BL 39, MW 149) are elevated with the highest $\delta^{238}\text{U}$ (0.56‰) and the highest U(VI) concentration (1.47 mg/mL) in PAA4 observed in BL 39, suggesting dissolution of the U ore and a lack of U(VI) reducing environments along this transect. This heterogeneous distribution of $\delta^{238}\text{U}$ in groundwater PAA4 suggests field scale heterogeneity in the distribution of naturally occurring reducing environments.

($^{234}\text{U}/^{238}\text{U}$) at Rosita. Extremely low ($^{234}\text{U}/^{238}\text{U}$) ranging from 0.69 to 0.82 in the Rosita U ore can be generated by (1) direct ejection of ^{234}U from the U mineral grains into the surrounding medium (i.e., groundwater) due to α -recoil, leading to a steady state depletion of ^{234}U in the U mineral grains and, (2) preferential dissolution of ^{234}U from the recoil-damaged lattice sites of U-bearing minerals. The fraction of ^{234}U ejected (f_α) directly from the U mineral into the surrounding medium is a function of size and geometry of mineral grains, and increases with decreasing grain size^{38,68,69}. If only direct recoil of ^{234}U is responsible for the observed ^{234}U depletion ($(^{234}\text{U}/^{238}\text{U}) \approx 0.75$), a corresponding ^{234}U loss factor or f_α of 0.25 is required. This value of f_α is expected only in sediments with a very fine grain size (0.2 – 2 μm)⁶⁸. The mean grain diameter of the 50% of the U minerals (D_{50}) in the Rosita ore is 12 μm (see Table S3). However, it is not uncommon that the amount of recoil loss is larger than expected based on the

geometric grain radius probably due to grain surface roughness⁶⁹. Furthermore, in U minerals, the extensive radioactive decay of U and intermediate daughter isotopes would likely result in much more lattice damage than observed in silicate minerals. Pervasive lattice damage may enhance preferential dissolution of ^{234}U in U minerals. Therefore, both direct recoil and dissolution of ^{234}U from the damaged lattice sites likely gave rise to observed ^{234}U depletion in the Rosita ore.

In many aquifers, the ($^{234}\text{U}/^{238}\text{U}$) of the groundwater reflects a balance between the supply of ^{234}U from α -recoil, preferential leaching, and the dissolution of the solids, which may contain ^{234}U depleted surfaces³⁴. The ore zone groundwater samples, except BL 8, exhibit the extreme ^{234}U depletion and ($^{234}\text{U}/^{238}\text{U}$) similar (average ($^{234}\text{U}/^{238}\text{U}$) = 0.76 ± 0.03 , $n = 9$) to that of the U ore. The average ($^{234}\text{U}/^{238}\text{U}$) values of the ore zone groundwater are within the uncertainty of that for the ore samples suggesting that dissolution within ore deposit is much more important than direct recoil of ^{234}U . Very high U content in U ore relative to that in groundwater results in a rapid shift in the isotopic composition toward that of the high-U solid in the ore zone. In contrast, Rosita groundwater samples with lower U concentrations have higher ($^{234}\text{U}/^{238}\text{U}$), consistent with aquifers where α -recoil dominates over dissolution of U from the bulk solids with lower U concentrations^{34,70,71}. Thus, the ($^{234}\text{U}/^{238}\text{U}$) composition of the ore zone groundwater adjusts to the value of the ore deposit, providing a means to trace ore zone water.

The spatial variation of ($^{234}\text{U}/^{238}\text{U}$) in groundwater along the hydraulic gradient may be understood using the framework described above. Compared to the ore zone groundwater, samples from the upgradient wells are more enriched in ^{234}U , but with ($^{234}\text{U}/^{238}\text{U}$) closer to the secular equilibrium value of 1, except in MW 129 and MW 53. The sediments upgradient of the ore zone have trace U concentrations primarily hosted in silicate minerals and possibly in

residual U minerals, deposited prior to the downgradient movement of the roll-front to its present location. In these older sediments with a low U content, α -recoil within the aquifer along with low rates of mineral dissolution might give rise to the slight ^{234}U enrichment in groundwater in the upgradient wells^{70,71}. Downgradient groundwater samples also show ^{234}U enrichment compared to the ore zone wells but are generally below secular equilibrium. This ^{234}U enrichment may be attributed primarily to the ^{234}U contribution from the downgradient sediments during transport. Typically, under pre-mining conditions, as the water exits the ore deposit, the U(VI) is reduced almost quantitatively toward the downgradient reduced edge of the roll-front. Sediments located further downgradient should have a U budget that is primarily in silicate minerals similar to the upgradient sediments. Thus due to efficient U removal over a relatively short distance from the ore zone, the ($^{234}\text{U}/^{238}\text{U}$) in the advecting water largely differs from that of the ore zone and evolves to a near secular equilibrium value during transport to the downgradient wells. At present, any influence of the ore zone groundwater with extremely low ($^{234}\text{U}/^{238}\text{U}$) is unlikely in the downgradient samples as $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Figure S4) suggest no apparent mixing between waters from the ore zone and downgradient wells.

($^{234}\text{U}/^{238}\text{U}$) as tracer for U migration. ($^{234}\text{U}/^{238}\text{U}$) in groundwater may be used to track U mobility along groundwater flow. Given the present groundwater velocity of 3 to 6 m yr⁻¹ at the site, it is unlikely that the post-mining restoration fluid has arrived at the downgradient monitoring wells, located approximately 200 m from the ore zone, since the cessation of the ISR mining between 1997 - 1999. In absence of efficient reduction of post-restoration high U(VI), the arrival of the ore zone water at the downgradient wells can be traced using the characteristic ($^{234}\text{U}/^{238}\text{U}$) (≈ 0.76) of the ore zone water. Therefore, if high U(VI) ore zone water escapes, it will

have a unique ($^{234}\text{U}/^{238}\text{U}$) signature that will persist according to the U(VI) concentration and the efficiency of (1) mixing with other water and (2) α -recoil and leaching processes downstream.

S isotopes as tracers for reduction and groundwater movement. The $\delta^{34}\text{S}$ values of sulfate in groundwater can help identify the processes influencing U mobility. Extremely depleted $\delta^{34}\text{S}$ of the Rosita U ore (-28.5‰ to -38.8‰) is similar to that reported for South Texas U ores (summarized in ref 8). These very low $\delta^{34}\text{S}$ values are generally attributed to redistribution of pre-ore FeS_2 produced by microbial sulfate reduction and mixing of groundwater with sulfur-enriched brine⁸. Although the $\delta^{34}\text{S}$ values in sulfate in Rosita groundwater vary over a wide range (11.8‰ to -19.9‰) (Figure S6), there is no systematic relationship between $\delta^{34}\text{S}$ and SO_4^{2-} concentrations in Rosita groundwater. When plotted against the groundwater U(VI) concentrations, a proxy for degree of dissolution and reduction, $\delta^{34}\text{S}$ in most of the ore zone BL wells plot in the same region (Figure S6). The characteristic depleted $\delta^{34}\text{S}$ values in ore zone groundwater likely result from the oxidative dissolution of sulfide minerals during which $\delta^{34}\text{S}$ in sulfate approaches the isotopic signature of the source sulfide. This dissolution signature is most prominent in samples from recently mined PAA3 ($\delta^{34}\text{S} = -14.8\text{‰}$ to -19.9‰).

The elevated $\delta^{34}\text{S}$ in aqueous sulfate is not likely to arise from microbial sulfate reduction and is consistent with mixing with ^{34}S enriched background water. The $\delta^{34}\text{S}$ values in groundwater from the PAA4, ranging from 3.2‰ to 6.6‰ , are significantly elevated above that in PAA3 wells. We did not observe any decrease in aqueous sulfate concentration or concomitant enrichment in $\delta^{34}\text{S}$ from ore zone to downgradient wells in PAA4. This suggests that $\delta^{34}\text{S}$ of aqueous sulfate in PAA4 represent the background S isotope signature of the site groundwater. In the mined part of the site, the samples with considerably high $\delta^{34}\text{S}$ enrichment up to 12‰ (e.g., BL 10, MW 45, MW 53, MW 102, MW 103, MW 137) also contain more than 12 mg/L

NO₃⁻, which precludes microbial sulfate reduction in these wells. The $\delta^{34}\text{S}$ in several downgradient samples, particularly in MW 37, MW 75, MW 89, and MW 137, approach 0.0‰ or occasionally higher values. In these wells, the redox potentials do not decrease below -105.5 mV and do not reach sulfate reducing conditions. Therefore, the elevated $\delta^{34}\text{S}$ in the mined part of the site is not indicative of sulfate reducing environments. However, we cannot completely rule out a minor amount of localized SO₄²⁻ reduction.

The characteristic depleted $\delta^{34}\text{S}$ of the ore zone wells may also be used as a tracer for the downgradient migration of the ore zone groundwater. However, any SO₄²⁻ reduction along the groundwater flow path would lead to enrichment of ³⁴S in the residual sulfate which would be difficult to distinguish from mixing with the downgradient groundwater enriched in ³⁴S. At present, we do not have any isotopic or geochemical evidence of major sulfate reducing areas in either un-mined or mined parts of the site, consistent with the measured Eh values. In the absence of substantial SO₄²⁻ reduction along the hydraulic gradient, characteristic S isotope ratios could be used to trace the mobility of the ore zone groundwater.

Implications for U remediation at Rosita ISR site. In the majority of the downgradient wells, lower $\delta^{238}\text{U}$ relative to the U ore and ore zone groundwater, accompanied by a decrease in U(VI) concentration, strongly suggest naturally occurring U(VI) reduction downgradient of the ore zone. Our results also suggest progressively stronger reducing environments ranging from nitrate to iron reducing conditions along the hydraulic gradient. The characteristic (²³⁴U/²³⁸U) signature may serve as a monitoring tool to trace fugitive ore zone water at Rosita in case of incomplete U(VI) reduction in the reducing environments located downgradient of the ore zone. Additionally, $\delta^{34}\text{S}$ signature may also be used as a tracer for the mobility of the ore zone groundwater. Overall, the implications of our findings should extend to all ISR sites similar to

Rosita. Although the isotopic and geochemical data from Rosita groundwater are effective in detecting naturally occurring U(VI) reduction at the ISR site, these data do not reveal the mechanism or the extent of U(VI) reduction. Future investigation will determine the potential, kinetics, and associated isotopic fractionation for U(VI) reduction in the downgradient sediments.

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Supporting Information. Details of the site background, analytical procedures, groundwater major ion and trace element concentrations, isotopic data ($\delta^{238}\text{U}$, ($^{234}\text{U}/^{238}\text{U}$), $\delta^{34}\text{S}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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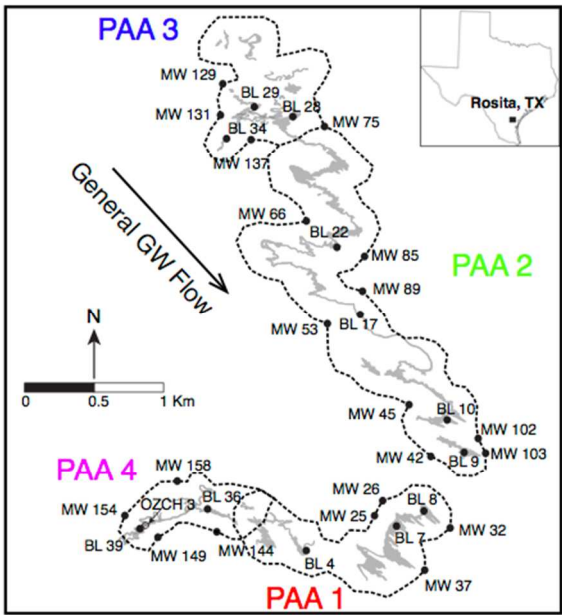


Figure 1. Map of the Rosita ISR site showing the sampling locations in the mining units (PAAs). The grey shaded area defines the U roll-front deposit. The dotted lines define the inferred PAA boundaries and the perimeter ring of the monitoring wells. Black dots show the sampling locations for the Base Line (BL) wells within the ore zone and upgradient and downgradient monitoring wells (MW). Arrow indicates the present groundwater flow direction. Open circle (OZCH3) shows the location of the U ore sample.

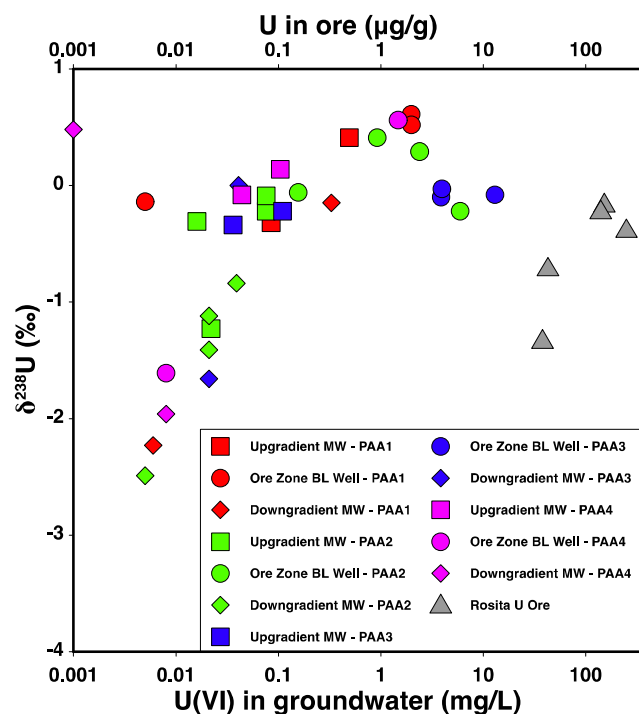


Figure 2. Measured $\delta^{238}\text{U}$ in Rosita groundwater and ore samples vs. U concentration. Red, green, blue and pink symbols represent the groundwater samples from PAA1, PAA2, PAA3, and un-mined PAA4, respectively. Grey triangles represent the U ore samples from PAA4. The error bars (2 s.e.) for $\delta^{238}\text{U}$ do not exceed the size of the symbols.

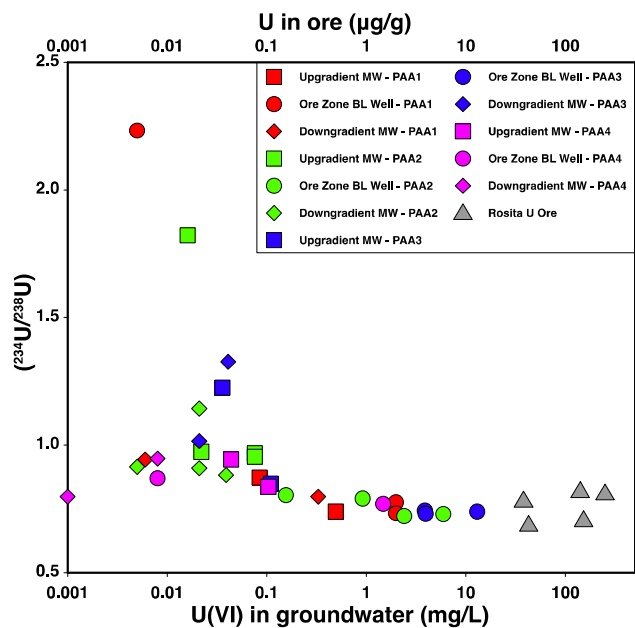
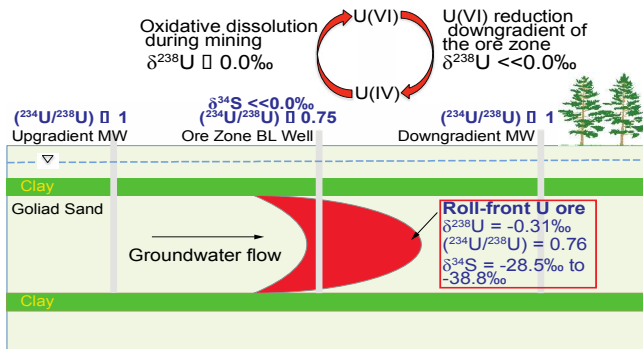
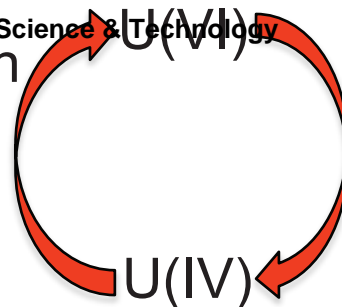


Figure 3. $(^{234}\text{U}/^{238}\text{U})$ vs. U concentration in Rosita groundwater and ore samples. Red, green, blue and pink symbols represent the groundwater samples from PAA1, PAA2, PAA3, and unmined PAA4, respectively. Grey triangles represent the U ore samples from PAA4. The error bars (2σ) for $(^{234}\text{U}/^{238}\text{U})$ are smaller than the size of the symbols.



TOC art

Oxidative dissolution
during mining
 $\delta^{238}\text{U} \geq 0.0\text{‰}$



U(VI) reduction
downgradient of
the ore zone
 $\delta^{238}\text{U} \ll 0.0\text{‰}$

